



Hydrodechlorination of chloromethanes with Pd on activated carbon catalysts for the treatment of residual gas streams

M.A. Álvarez-Montero, L.M. Gómez-Sainero ^{*}, M. Martín-Martínez, F. Heras, J.J. Rodríguez

Área de Ingeniería Química, Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain

ARTICLE INFO

Article history:

Received 11 December 2009

Received in revised form 28 January 2010

Accepted 4 February 2010

Available online 11 February 2010

Keywords:

Hydrodechlorination

Residual gases

Dichloromethane

Chloroform

Monochloromethane

Pd/activated carbon catalysts

ABSTRACT

Laboratory-prepared Pd/C catalysts have been investigated in the deep gas-phase hydrodechlorination (HDC) of monochloromethane (CH_3Cl), dichloromethane (CH_2Cl_2) and trichloromethane (CHCl_3). The catalysts were found to be active in HDC, the reactivity following the order $\text{CHCl}_3 > \text{CH}_2\text{Cl}_2 > \text{CH}_3\text{Cl}$. Selectivities to non-chlorinated compounds were found to be higher than 90% in most cases. The results obtained with the catalyst prepared from PdCl_2 suggest that all the reaction products are primary products. The CH_4 , CH_3Cl and CH_2Cl_2 come from the hydrogenation of the corresponding adsorbed chloride radical, while hydrocarbons of more than one carbon atoms are formed by reaction and subsequent hydrodechlorination of two radicals adsorbed in neighbouring active centers. The catalyst undergoes a significant deactivation which appears to be due to the poisoning of active centers with chlorinated hydrocarbons. The use of $\text{Pd}(\text{NO}_3)_2$ as Pd precursor leads to a decrease in the activity due to its lower Pd dispersion and a lower proportion of electrodedeficient Pd species.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Chlorinated volatile organic compounds are commonly used as solvents and reactants in chemical and pharmaceutical industries. They are also employed in producing aerosols, adhesives, and for dry cleaning, etc. [1]. However, because of their high toxicity and carcinogenic character these compounds are classified nowadays among the most hazardous atmospheric pollutants [2,3]. In particular, chloroform and dichloromethane are included in the U.S. EPA's Toxic Release Inventory (TRI). Moreover, the emission of organic chlorinated compounds to the atmosphere contributes to the destruction of the ozone layer, to the formation of photochemical smog and to global warming [2–4]. Emission of these compounds is restricted by environmental regulations. This leads to the necessity of developing effective technologies for the treatment of residual streams contaminated with these pollutants. Catalytic hydrodechlorination (HDC) has, thus, become one of the most promising emerging technologies. HDC has potential economic and environmental advantages over other methods, because it operates at low temperatures and atmospheric pressure, and the reaction products are less hazardous than those resulting from other techniques [1,5–7].

There is a growing literature devoted to the hydrodechlorination of organochlorinated compounds with catalysts based on

different metals and supports. However, in the case of chloromethanes most of the publications refer to carbon tetrachloride [6,8–14] and many of them are focused on the production of chloroform [8–12,15]. There are scarce publications devoted to the deep hydrodechlorination of chloroform (TCM), dichloromethane (DCM) and monochloromethane (MCM) [16–23], and almost none of them involves using carbon as a catalyst support [20] and low concentrations of contaminants [22,23], which happen to be the most common situation for residual gas effluents. On the other hand, the catalysts reported in these studies suffer a significant deactivation and the causes of catalyst deactivation have been scarcely investigated.

Pd supported catalysts are commonly reported to exhibit the highest activity in the complete dehalogenation of chloromethanes, but they suffer a fast deactivation. Aristizabal et al. [22] tested different catalysts based on Pd and Ni over several supports (SiO_2 , TiO_2 , ZrO_2 and Al_2O_3) and synthesized by different methods (cogellation and impregnation) for the gas-phase hydrodechlorination of DCM at a concentration of 1200 ppm. Pd catalysts prepared by impregnation were more active and selective. Pd/TiO₂ was the most active, though this catalyst underwent a strong deactivation. In comparison, Pd/SiO₂ showed a moderate activity and a higher resistance to deactivation than other catalysts. However, acceptable activity was maintained for only 48 h. Mori et al. [17] reported that Pd/SiO₂ showed high activity at 200 °C and atmospheric pressure. Lopez et al. [18] studied the hydrodechlorination of several organochlorides (DCM, tetrachloroethylene, chlorobenzene and 1,2-dichlorobenzene), all

* Corresponding author. Tel.: +34 914976939; fax: +34 914973516.
E-mail address: luisa.gomez@uam.es (L.M. Gómez-Sainero).

of them alone and in mixtures, over Pd/Al₂O₃ catalyst. The reported DCM conversions were lower than 30% in all the cases although the selectivities obtained toward non-chlorinated species were higher than 95%. Prati and Rossi [19] tested different metals (Pd and Pt) in the hydrodechlorination of chloromethanes and reported that the best results were obtained with Pd. Some other papers have reported the HDC of TCM and DCM with precious metals catalysts (Pd/Al₂O₃, Pt/Al₂O₃, Rh/Al₂O₃, Pt/C, Pd/SiO₂, etc.) [5,20,21]. However, all these studies have been carried out in liquid phase or at high concentrations, and none of them has investigated the causes of catalyst deactivation which limits technological application.

In a previous study, gas-phase hydrodechlorination of DCM with commercial and laboratory-prepared Pd on activated carbon (Pd/C) catalysts gave very good results of activity and selectivity to non-chlorinated products, but the catalysts used underwent significant deactivation [1].

In this contribution, the activity, selectivity and stability of several laboratory-made 1.0% (w/w) Pd/C catalysts have been investigated for the gas-phase hydrodechlorination of three chloromethanes, TCM, DCM and MCM. A reaction scheme is proposed for HDC and the possible causes of catalyst deactivation are analysed.

2. Experimental

2.1. Catalyst preparation

Two palladium catalysts supported on a commercial activated carbon (supplied by Erkimia S.A. whose characteristics have been reported elsewhere [24]) were prepared by incipient wetness impregnation. One of the catalysts (PdCCl) was prepared using aqueous solutions of H₂PdCl₄ (from anhydrous PdCl₂ supplied by Sigma-Aldrich) with appropriate concentrations to obtain 1 wt% Pd nominal load, using a carbon particle size of 0.25–0.5 mm. In order to analyze the effect of the palladium precursor, another catalyst (PdCN) was prepared in the same way but using Pd(NO₃)₂ (Fluka) as precursor of the active phase and the same carbon particle size. The samples were dried overnight at room temperature and heated up to 100 °C at a heating rate of 20 °C/h, maintaining the final temperature for 2 h. The activation of both catalysts was carried out by reduction under continuous H₂ flow. The samples were heated up to 250 °C at a heating rate of 10 °C/min and maintained at that temperature for 2 h. Hydrogen was supplied by Praxair with a minimum purity of 99.999%.

2.2. Catalyst characterization

The porous structure of the catalysts was characterized from the 77 K N₂ adsorption–desorption isotherms using a Quanta-chrome Autosorb 6B apparatus. The samples were previously outgassed for 4 h at 250 °C and a residual pressure of 10^{−3} Torr.

The bulk palladium content was determined via inductive coupled plasma-mass spectroscopy (ICP-MS) in a PerkinElmer model Elan 6000 Scieix system that was equipped with an autosampler (PerkinElmer model AS-91). The samples were previously digested for 15 min in a microwave oven, using a strong acid mixture at 180 °C.

The X-ray diffraction (XRD) patterns of the catalysts and supports were obtained in a X'Pert PRO Panalytical Diffractometer. The powdered sample was scanned using Cu K α monochromatic radiation ($\lambda = 0.15406$ nm) and a Ge Mono filter. A scanning range of $2\theta = 10$ –100° and scan step size of 0.020° with 5 s collection time were used. The diffractograms were compared with the JCPDS-ICDD references for identification purposes.

The surface of the catalysts was analyzed by X-ray photoelectron spectroscopy (XPS) with a Physical Electronics 5700C Multi-technique System, using Mg K α radiation ($h\nu = 1253.6$ eV). To determine all the elements present on the catalyst surface, general spectra were recorded for the samples, by scanning up to a binding energy (BE) of 1200 eV. The BE of the Pd 3d_{5/2} core level and full width at half maximum (FWHM) values were used to determine the chemical state of Pd. The BE of the Cl 2p spectra was used to analyse the chemical state of Cl. Correction for binding energies due to sample charging was done by taking the C 1s peak (284.6 eV) as an internal standard. The accuracy of the BE scale was ± 0.1 eV. The data analysis procedure involved smoothing, a Shirley background subtraction and curve fitting using mixed Gaussian–Lorentzian functions by a least-squares method. The atomic ratios of the elements were calculated from the relative peak areas of the respective core level lines using Wagner sensitivity factors [25].

A Micromeritics ChemiSorb 2705 pulse analyzer was used to measure the accessibility of the surface sites by CO chemisorption at room temperature. The sample (0.15–0.30 g) was first reduced at 250 °C for 2 h under hydrogen flow and then cooled under helium flow at room temperature. Several pulses of 50 μ L CO were then introduced until the saturation of the catalyst surface was achieved. The number of exposed palladium atoms was calculated from CO chemisorption data. The stoichiometry of the adsorption of CO over palladium atoms was assumed to be 1 [26–29].

2.3. Catalytic activity experiments

The activity of the catalysts in the hydrodechlorination of the chloromethanes was evaluated in a continuous flow reaction system described elsewhere [1], consisting essentially of a 9.5 mm i.d. fixed bed micro-reactor, coupled to a gas chromatograph with a FID detector for the analysis of the reaction products.

The HDC experiments were performed at atmospheric pressure using a total flow rate of 100 N mL/min, and a H₂/chloromethane molar ratio of 100. The gas feed, with a chloromethane concentration of 1000 ppm, was prepared by mixing adequate proportions of the starting chloromethane/N₂ commercial mixture and N₂. The catalyst weight and temperature were adjusted to the desired values in each run. Space-times in the range of $\tau = 0.08$ –1.73 kg h mol^{−1} and temperatures of 150–250 °C were tested. The behavior of the catalysts was analyzed in terms of chloromethane conversion and selectivities to the different reaction products. The evolution of the catalytic activity upon time on stream was also monitored.

3. Results and discussion

3.1. Characterization of the catalysts

Table 1 summarizes the BET surface area, pore volume, bulk Pd content and the Pd dispersion values of the fresh catalysts as well as those of PdCCl catalyst after being used in the hydrodechlorination of DCM.

The 77 K N₂ adsorption–desorption isotherms of the catalysts approached to Type I of the BDDT classification, being indicative of

Catalyst	Palladium content (%)	S _{BET} (m ² /g)	Micropore volume (cm ³ /g)	D (%)
PdCCl	0.86	1236	0.49	38.1
PdCN	0.81	1255	0.44	26.1
PdCCl used ^a	0.85	1282	0.53	9.4

^a In HDC of DCM at 250 °C and 1.73 kg h mol^{−1} of space time, after 100 h time on stream.

microporous solids, although a contribution of mesopores is also present to some extent. All of them show a high BET surface area, with values well above $1200 \text{ m}^2/\text{g}$, even for the used catalyst, indicating that constriction or partial blockage of the porous structure do not occur upon reaction, at the relatively mild temperatures used in the experiments.

The fresh catalysts show a good Pd dispersion, although significantly lower when using Pd nitrate as precursor, which some authors have attributed to the existence of a different type of adsorption sites [30]. Selecting a suitable Pd precursor appears to be decisive for obtaining highly dispersed Pd catalysts. The use of acid solutions of Pd chloride leads to the formation of tetrachloropalladic acid which strongly interacts with the surface of carbon through the adsorption equilibrium $\text{PdCl}_4^{2-} + \text{A} \leftrightarrow \text{PdCl}_{(4-n)}^{(2-n)-} \text{A} + n\text{Cl}^-$. According to these authors, this leads to the formation of small Pd particles homogeneously distributed in the pores of the catalyst with electrodeficient palladium. In contrast, when $\text{Pd}(\text{NO}_3)_2$ is used as precursor, Pd is more weakly deposited and occurs predominantly on the external surface. A significant decrease in the Pd dispersion was observed for the used PdCCl catalyst which can be attributed to the poisoning of the active centers with reactants, intermediates and/or reaction products as suggested by the characterization results presented forward in this paper.

Fig. 1 shows the XRD profiles of the PdCCl catalyst reduced and after used in the HDC of DCM. A peak at 2θ value of 40° is observed in the fresh sample which corresponds to Pd particles in the cubic system. The pattern of the used catalyst shows a peak of similar intensity suggesting that the decrease in the Pd dispersion cannot be attributed to metal sintering occurring at the reaction conditions. Nevertheless, a shift to a lower 2θ value of 39° is observed, assessed by some authors to a metal phase change through the formation of a Pd–C solid solution, upon use of Pd/C

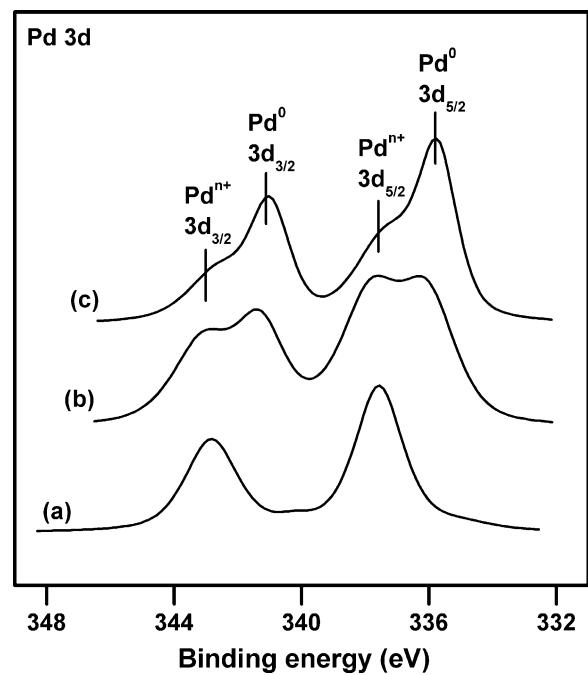


Fig. 2. Pd 3d core level XPS spectra of PdCCl catalyst: (a) as prepared; (b) after reduction in H_2 at 250°C ; (c) after used in HDC of DCM.

catalysts in similar reactions [31]. The larger peaks observed in the XRD profiles, corresponding to 2θ values of 26.4° , 43.5° and 81.4° , come from the support.

Fig. 2 shows the XPS profiles of as prepared and reduced fresh PdCCl catalyst, as well as after being used. In agreement with

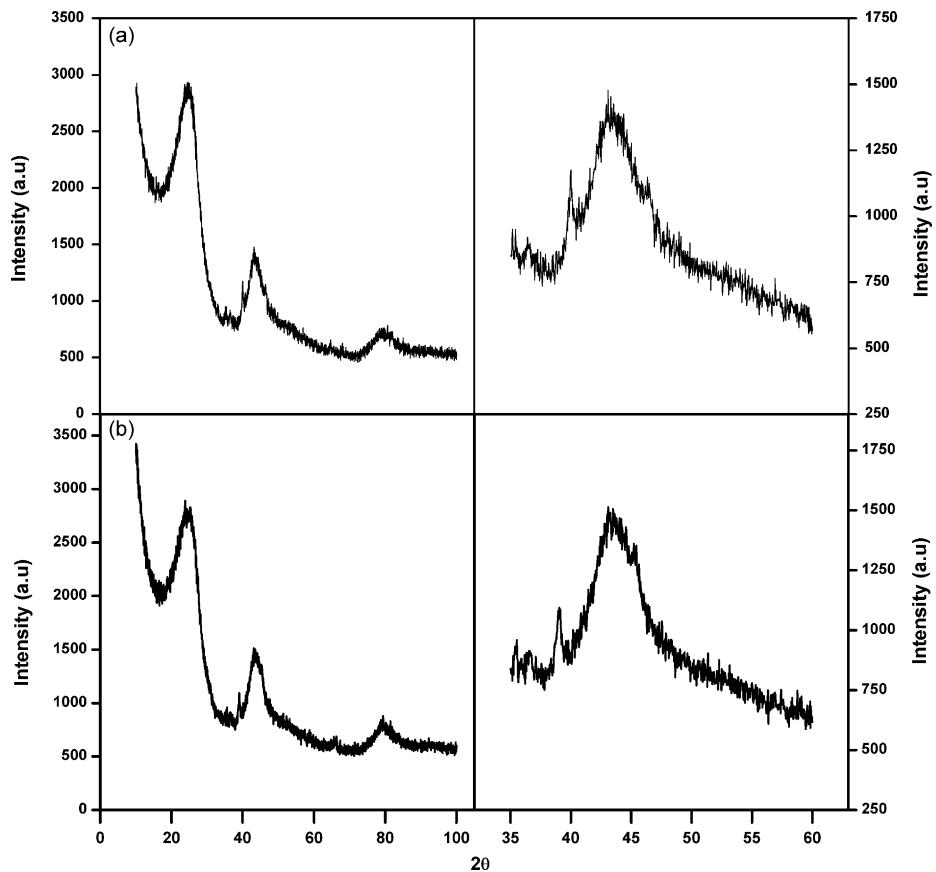


Fig. 1. XRD patterns of PdCCl catalyst: (a) after reduction in H_2 at 250°C ; (b) after used in HDC of DCM.

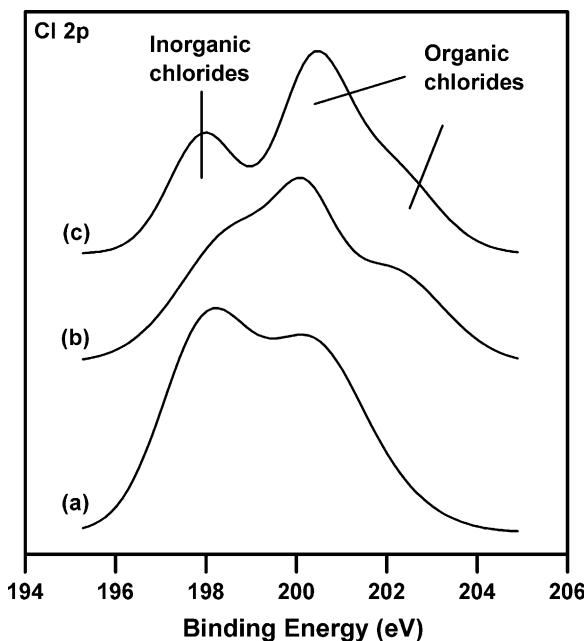


Fig. 3. Cl 2p core level XPS spectra of PdCl catalyst: (a) as prepared; (b) after reduction in H_2 at $250^\circ C$; (c) after used in HDC of DCM.

previous studies [1,24], core level spectra of Pd 3d orbitals show the existence of mainly electrodeficient Pd in the as prepared catalyst, and these species together with Pd^0 in the reduced sample. A main band centered at a binding energy of 337 eV was observed for $Pd 3d_{5/2}$ in the as prepared unreduced catalyst. Two main bands centered at binding energy values around 335.5 eV and 337 eV were observed for $Pd 3d_{5/2}$ in the reduced catalyst, which can be attributed to metallic palladium (Pd^0) and electro-deficient palladium (Pd^{n+}), respectively. Integration of the areas under the curves yields fairly similar relative proportions of these two species as it was found in previous studies [1,24]. The use of the catalyst in the HDC reaction leads to a decrease of the proportion of electrodeficient Pd (Fig. 2c).

The Cl 2p XPS spectra of the as prepared, reduced and used PdCl catalyst are shown in Fig. 3. Three main bands are observed at binding energies of 198.0, 200.2 and 201.2 for as prepared catalyst, 198.6, 200.2 and 202.1 eV for the reduced catalyst and 198.0, 200.4 and 202.1 eV for the used one. Binding energies of 198.6 and 198.0 eV correspond to inorganic chlorides while the other ones correspond to organic chlorides. The amount of inorganic chloride highly decreases after reduction as H_2PdCl_4 was used as the precursor, as well as the organic chloride one, which comes from the carbon surface. On the other hand, the amount of organic chloride in the catalytic surface highly increases (37%) upon use in HDC. In accordance with the dispersion results, poisoning of active centers with chlorocarbon compounds seems to take place.

Significant differences were found in the spectra of the PdCN catalyst (Fig. 4). In the sample of PdCN prior to reduction, the presence of the two species of Pd, electrodeficient and zerovalent, can be observed. Core level spectra of Pd 3d_{5/2} orbital shows two main bands centered at 337.19 eV and 335.3 eV, respectively. This is an evidence of partial reduction of the PdCN catalyst during the impregnation process, which leads to a lower Pd dispersion (Table 1) in agreement with the findings of different authors [24,30]. In consequence, the higher proportion of reduced species in the starting as-prepared PdCN catalyst, in addition to the weaker interaction of Pd with the support, leads to a much higher proportion of Pd in reduced state in the final catalyst (once reduced

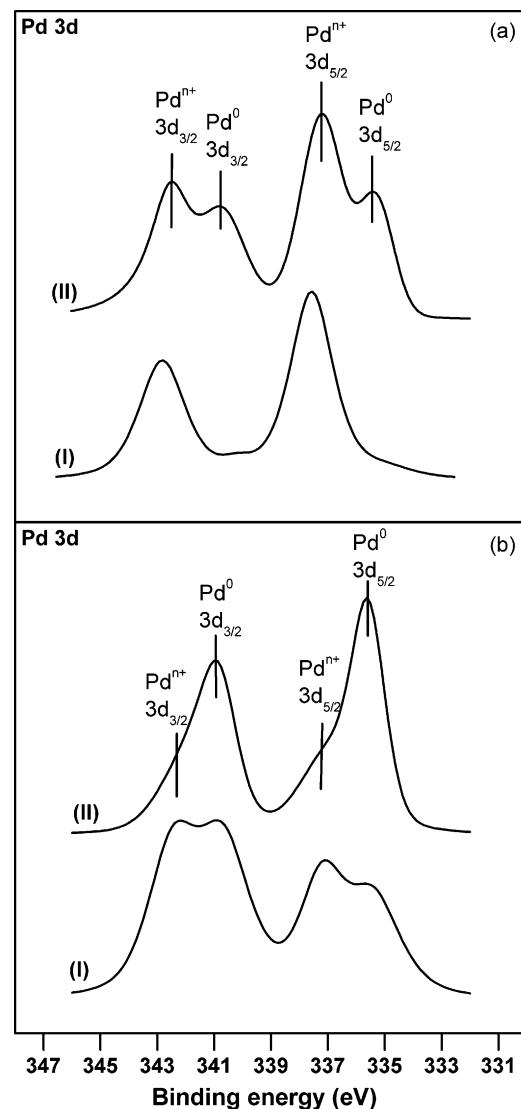


Fig. 4. Pd 3d core level XPS spectra of as prepared (a) and after reduction in H_2 at $250^\circ C$ (b) catalysts: (I) PdCl; (II) PdCN.

in H_2 atmosphere), which highly affects its activity, as it will be seen later.

3.2. Activity and selectivity of the PdCl catalyst and the reaction scheme

Fig. 5 shows the evolution of MCM, DCM and TCM conversion with space-time at different reaction temperatures. In all cases, the reactivity highly increases with the chlorine content of the molecule, following the sequence $CHCl_3 > CH_2Cl_2 > CH_3Cl$. This is in agreement with the results obtained by other authors [17].

As can be seen in Fig. 5a, MCM conversion although increasing with temperature and space-time, remains in fairly modest values within the wide ranges of both variables investigated. Less than 35% conversion was achieved at the highest temperature and space-time. Fairly higher conversion values were obtained in the hydrodechlorination of DCM (Fig. 5b) although only at the highest temperature tested ($250^\circ C$) those values exceeded 90%. As expected, TCM showed by far the highest reactivity among the chloromethanes investigated. Almost complete conversion was reached at relatively low space-time even at $125^\circ C$ (Fig. 5c).

In the HDC of MCM, methane was the only reaction product detected. The products distribution from HDC of DCM and TCM are

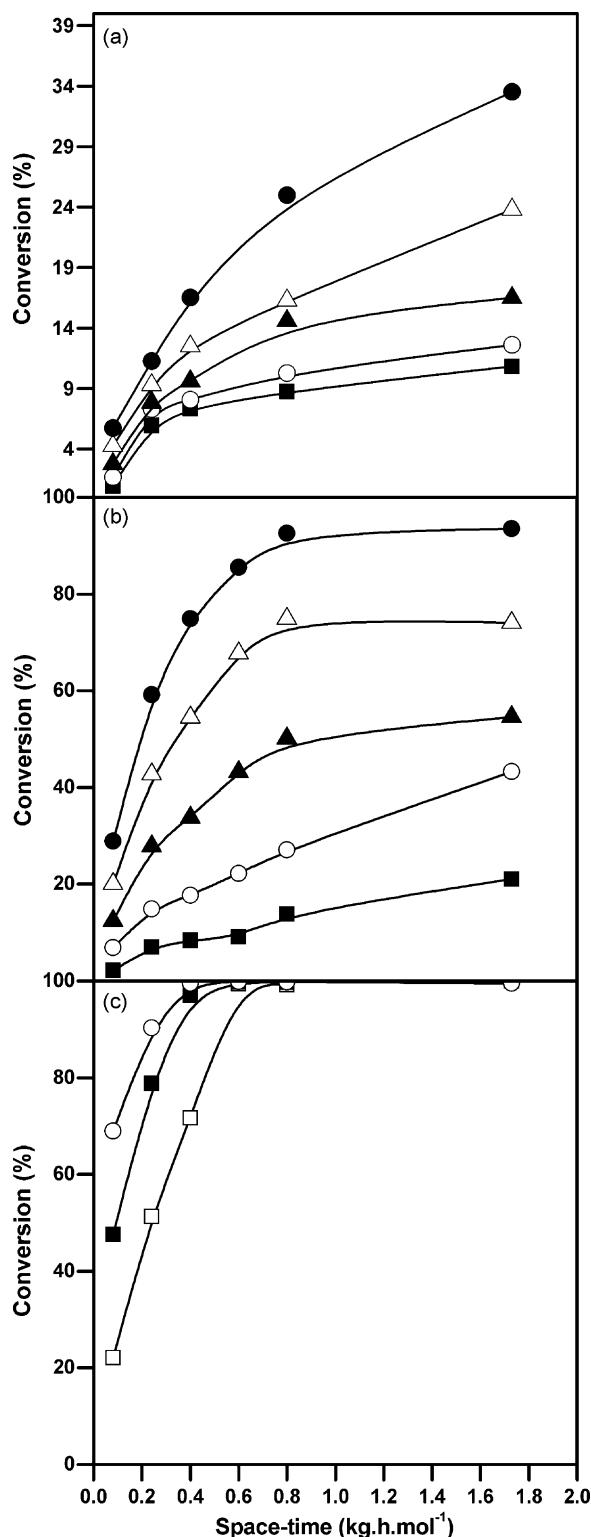


Fig. 5. HDC of MCM (a); DCM (b) and TCM (c) with PdCl catalyst at different temperatures ($^{\circ}\text{C}$): (□) 125; (■) 150; (○) 175; (▲) 200; (●) 250.

summarized in Tables 2 and 3, respectively. A wider diversity of the reaction products was obtained as the chlorine content of the molecule increases. On the other hand, the selectivity to methane highly diminishes when increasing the chlorine content, being the only reaction product in the case of MCM, as indicated before. In all cases the selectivity to non-chlorinated products is fairly high. The low selectivity to methane observed in the HDC of TCM is not

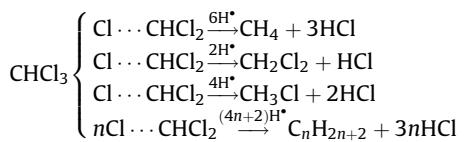
associated with a high selectivity to chlorinated products but to hydrocarbons up to C_4 . Moreover, the overall selectivity to chlorinated products is significantly lower in the HDC of TCM than in the case of DCM, although both DCM and MCM are obtained from the former.

In the HDC of DCM, methane is by far the main reaction product. The selectivity to MCM decreases as the temperature increases, being lower than 10% beyond $200\text{ }^{\circ}\text{C}$. Small amounts of ethane and propane were also obtained. As can be observed (Table 2), the temperature has a significant effect on products distribution, while space-time is much less important in this respect. Selectivity to hydrocarbons higher than C_1 (chiefly ethane with very low amounts of propane) is favoured by increasing the temperature to the detriment of methane and MCM.

In the HDC of TCM (Table 3), it is important to notice the high selectivity to non-chlorinated compounds, always well above 90% and in most cases higher than 95%. Methane was again the main reaction product but now close percentages of ethane were obtained together with significant amounts of propane and even butane. Small quantities of ethylene and propylene were also found at low space-times. As with DCM, space-time shows no significant effect in products distribution while it is more affected by temperature. As can be seen, the selectivity to hydrocarbons higher than C_1 increases when increasing the reaction temperature, to the detriment of methane and DCM.

Fig. 6 shows the evolution of the products yield and selectivity with space time at a reaction temperature of $150\text{ }^{\circ}\text{C}$. It can be observed that all the species have a finite rate of formation from TCM at zero space-time (Fig. 6a), which indicates that all are primary products formed from the chloroform-derived chloride radical. Consequently, the selectivities to all the products show positive intercepts when extrapolating to zero space-time (Fig. 6b).

As stated in previous studies [1,24,32], the HDC reaction proceeds through the dissociative adsorption of both the corresponding chloromethane and H_2 on the catalyst surface. Thus, the following reaction scheme can be proposed for TCM:



Methane, MCM and DCM would be formed from the hydrogenation of the adsorbed dichloromethane radical, while condensation products would proceed from the reaction of two or more adsorbed radicals and hydrogen.

The selectivities to MCM and DCM are roughly constant within the wide range of space-time tested (Fig. 6b), confirming that methane is exclusively produced from TCM in one step, without desorption of the intermediates. As the simultaneous substitution of the three Cl atoms by three H atoms seems to be difficult, substitution by a concerted mechanism was proposed in a previous work for carbon tetrachloride hydrodechlorination [32]. The concerted mechanism has been proposed to be a true consecutive process that takes place in the adsorbed phase on the same active center *via* a “rake-type” mechanism [33–36] in which the intermediate species remain adsorbed. Thus, the extremely fast and stepwise substitution of Cl atoms, from the Cl-surface complexes, by H atoms from $^{\bullet}\text{H}$, proceeds until the adsorbed precursor of methane ($^{\bullet}\text{CH}_4$) is formed, which desorbs as the stable final product of this surface sequential path while the stoichiometric amount of HCl is produced. It should be considered that this sequence in the *rake-type* mechanism does not involve any real physical translation of the surface species. It merely represents the progressive change that the intermediate adsorbed complex undergoes evolving along the reaction coordinate, from $\text{Cl}^{\bullet}\text{CHCl}_2$

Table 2Products distribution in the HDC of DCM with PdCl_3 catalyst.

τ (kg h mol $^{-1}$)	T (°C)	Selectivity (%)				τ (kg h mol $^{-1}$)	T (°C)	Selectivity (%)			
		CH_4	C_2H_6	C_3H_8	CH_3Cl			CH_4	C_2H_6	C_3H_8	CH_3Cl
0.08	150	84.3	0.0	0.0	15.7	0.6	150	79.9	3.1	0.0	17.0
	175	78.0	9.4	0.0	12.6		175	78.9	7.5	0.0	13.6
	200	74.5	15.6	0.0	9.9		200	75.8	12.7	0.7	10.8
	225	68.0	22.3	1.7	8.0		225	70.5	19.8	1.1	8.6
	250	62.7	27.9	2.2	7.2		250	64.5	26.6	1.6	7.3
0.24	150	81.5	2.9	0.0	15.6	0.8	150	79.5	3.1	0.0	17.4
	175	79.0	8.4	0.0	12.6		175	78.9	7.2	0.0	13.9
	200	75.0	14.0	0.8	10.2		200	76.0	12.4	0.6	11.0
	225	69.5	20.8	1.3	8.4		225	70.9	19.2	1.1	8.8
	250	63.4	27.4	1.9	7.3		250	64.8	26.5	1.6	7.1
0.4	150	79.5	3.5	0.0	17.0	1.73	150	79.3	2.1	0.0	18.6
	175	78.8	7.7	0.0	13.5		175	79.2	5.9	0.0	14.9
	200	75.4	13.1	0.7	10.8		200	77.4	10.4	0.5	11.7
	225	70.0	20.1	1.2	8.7		225	73.6	16.6	0.8	9.0
	250	63.6	27.3	1.8	7.3		250	67.9	23.9	1.4	6.8

to ${}^*\text{CH}_4$, on the same active site. Thus, this mechanism could explain how methane appears as a primary product from CHCl_3 in spite of the fact that transformation of three C–Cl bonds into three C–H bonds is involved.

The overall selectivity to hydrocarbons higher than C_1 in general decreases somewhat as the space-time increases. In recent studies analyzing the nature and role of the Pd active centers in this reaction [1,24], we found that they are dual in nature and constituted by the association of neighbouring metallic and electron deficient palladium species: $[\text{Pd}^0 + \text{Pd}^{n+}]$. Hydrogen chemisorbs and homolytically dissociates on Pd^0 to give the adatom $\text{Pd}-\text{H}$ (H^*), whereas the chloromethane chemisorbs on a single Pd^{n+} site. The formation of the condensation products implies the reaction of two adsorbed chloride radicals, so that the lower concentration of reactant at higher space-times leads to a greater difficulty of finding an adsorbed reactant in the vicinity, leading to a decrease of condensation products selectivity. Correspondingly, the higher proportion of hydrogen relative to the chloride species adsorbed, results in a slight increase of methane selectivity as the space-time increases.

The fact that methane was the only reaction product in the hydrodechlorination of MCM is another evidence of the formation of condensation products through the intermediate organochlor-

ide radicals. The dissociative adsorption of MCM leads to the non-chlorinated intermediate $\text{CH}_3\cdot$, which seems of low reactivity for the formation of condensation products. The wider distribution of condensation products as the number of chlorine atoms of the chloromethane increases is consistent with the reaction scheme proposed since the reactivity increases with the chlorine content [17].

3.3. Influence of the Pd precursor

When $\text{Pd}(\text{NO}_3)_2$ was used as Pd precursor instead of PdCl_2 , the conversion values decreased for the three chloromethanes investigated (Fig. 7). It can be partially attributed to the lower Pd dispersion of PdCN catalyst (Table 1). Differences in the state of Pd were evidenced by XPS (Fig. 4). The catalyst prepared from $\text{Pd}(\text{NO}_3)_2$ exhibits a lower proportion of electrodeficient Pd which seems to be important for the activity of the catalysts. The effect of the Pd precursor is more clearly seen in the HDC of DCM (Fig. 7). On the opposite, the Pd precursor shows a slight influence in the selectivity to chlorinated compounds. Slightly higher selectivities to chlorinated products in DCM hydrodechlorination were obtained when $\text{Pd}(\text{NO}_3)_2$ was used as Pd precursor (Fig. 8), whereas in the case of MCM, methane is the only reaction product

Table 3Products distribution in the HDC of TCM with PdCl_3 catalyst.

τ (kg h mol $^{-1}$)	T (°C)	Selectivity (%)							
		CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	C_4H_{10}	CH_2Cl_2	CH_3Cl
0.08	125	44.7	30.7	1.0	13.2	0.0	5.7	3.4	1.3
	150	39.4	33.6	1.1	14.8	0.5	6.6	2.6	1.4
	175	32.7	36.4	1.8	16.2	0.9	7.5	3.0	1.5
0.24	125	48.6	30.1	0.4	11.2	0.0	4.3	4.5	0.9
	150	44.6	33.0	0.4	12.6	0.0	5.0	3.4	1.0
	175	37.2	37.1	0.6	14.4	0.2	6.0	3.3	1.2
0.4	125	48.5	30.0	0.0	10.9	0.0	4.0	5.1	1.5
	150	45.4	32.9	0.0	12.1	0.0	4.6	3.7	1.3
	175	37.8	37.6	0.0	14.5	0.0	5.9	3.5	0.9
0.6	125	52.7	28.3	0.0	8.9	0.0	3.0	4.7	2.4
	150	47.8	32.6	0.0	11.1	0.0	3.9	3.0	1.6
	175	41.4	37.4	0.0	12.9	0.0	4.7	2.5	1.1
0.8	125	50.6	29.7	0.0	10.2	0.0	3.4	4.8	1.3
	150	45.8	33.2	0.0	12.2	0.0	4.7	3.2	0.9
	175	38.2	37.8	0.0	14.4	0.0	5.8	2.9	0.9
1.73	150	49.1	30.9	0.0	11.0	0.0	4.2	4.0	0.8
	175	42.7	34.5	0.0	13.3	0.0	5.3	3.0	1.2

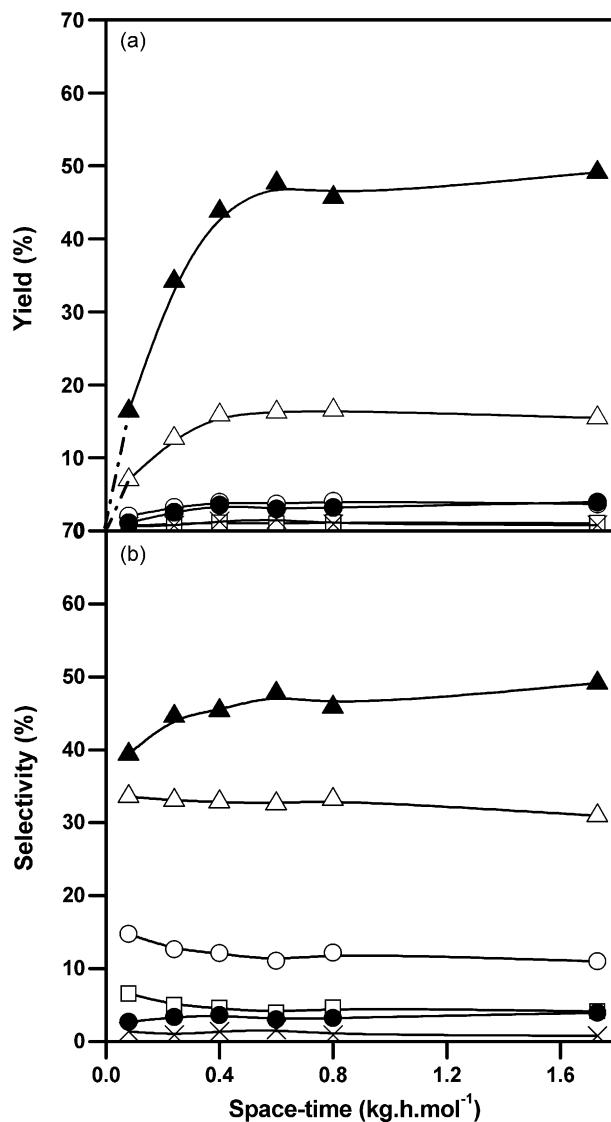


Fig. 6. Effect of space-time in the yield (a) and selectivity (b) to reaction products in the HDC of TCM with PdCCl catalyst at a reaction temperature of 150 °C: (▲) CH₄; (△) C₂H₆; (○) C₃H₈; (□) C₄H₁₀; (×) MCM; (●) DCM.

obtained with both catalysts. Selectivity to methane increases when using Pd(NO₃)₂ as precursor to the detriment of hydrocarbons with two or more carbon atoms, the effect being more pronounced in the case of TCM. This confirms that electrodeficient Pd is involved in the formation of condensation products. From the mechanism proposed above, as the choromethane is preferentially adsorbed on electrodeficient Pd, reaction of the species adsorbed on two or more of these sites is necessary for the formation of hydrocarbons higher than C₁, while the amount of Pdⁿ⁺ is greatly decreased in PdCN catalyst (Fig. 4).

3.4. Catalyst deactivation

Fig. 9 shows the evolution of conversion of the three chloromethanes upon time on stream in long-term experiments with the PdCCl catalyst. Space time and temperature of 0.24 kg h mol⁻¹ and 150 °C, respectively, were used in the case of TCM and 1.73 kg h mol⁻¹ and 250 °C for MCM and DCM. A loss of activity is observed in all the cases although significantly less pronounced in the case of TCM. As discussed before, no significant constriction of the porous structure occurred under the operating

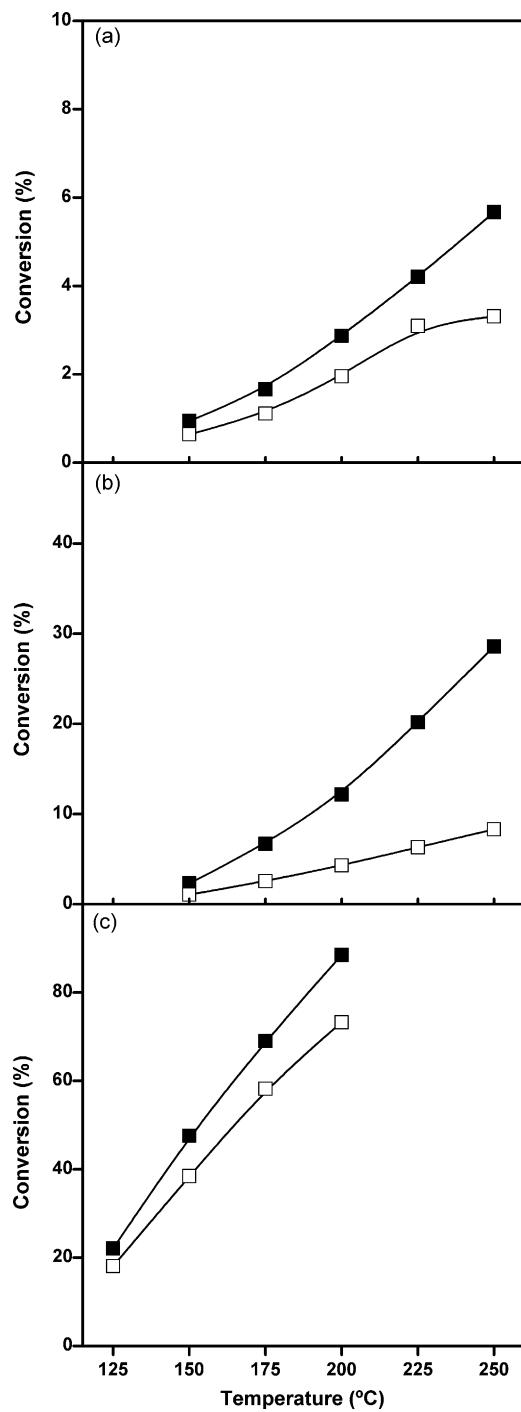


Fig. 7. Influence of the Pd precursor in the HDC of MCM (a), DCM (b) and TCM (c): (■) PdCCl; (□) PdCN.

conditions of the experiments (see Table 1). CO chemisorption showed a significant decrease in the amount of accessible Pd after 100 h time on stream of DCM hydrodechlorination (see Table 1).

Looking at the XRD profiles of the catalysts (Fig. 1), this reduction is not likely to be due to the sintering of Pd particles since no differences in size were found between the fresh and used catalyst. The analysis of the Pd XPS spectra of the used PdCCl catalyst showed a decrease in the proportion of the electrodeficient Pd (Fig. 2). Considering that the dissociative adsorption of chloromethane takes place on that Pd species, deactivation can be mainly attributed to the poisoning of the active centers by reactant and/or reaction products, which cause a reduction of the accessible

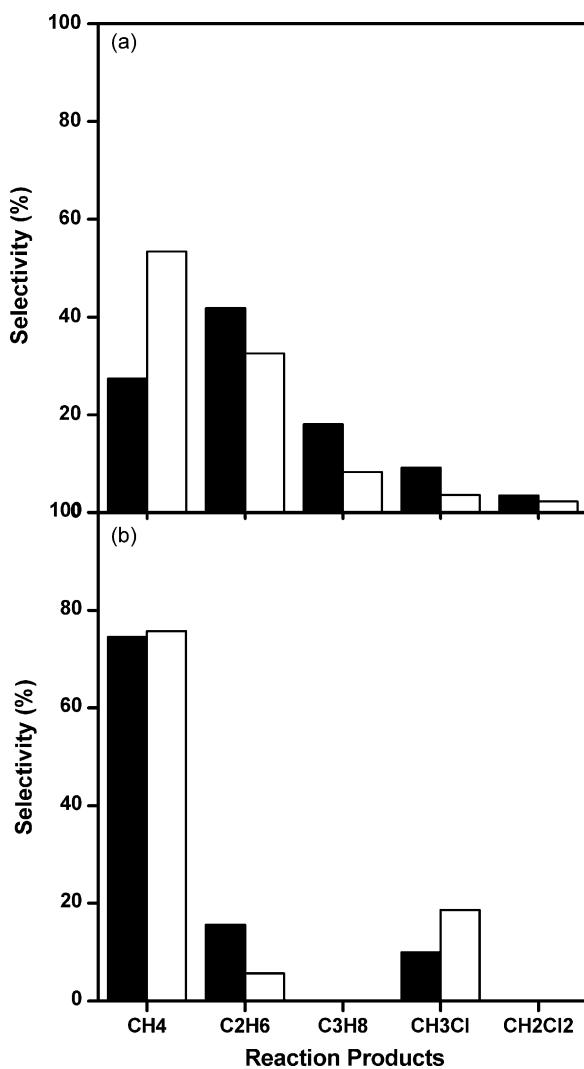


Fig. 8. Influence of the Pd precursor on the products distribution in the HDC of TCM (a) and DCM (b) at 200 °C: (■) PdCCl; (□) PdCN.

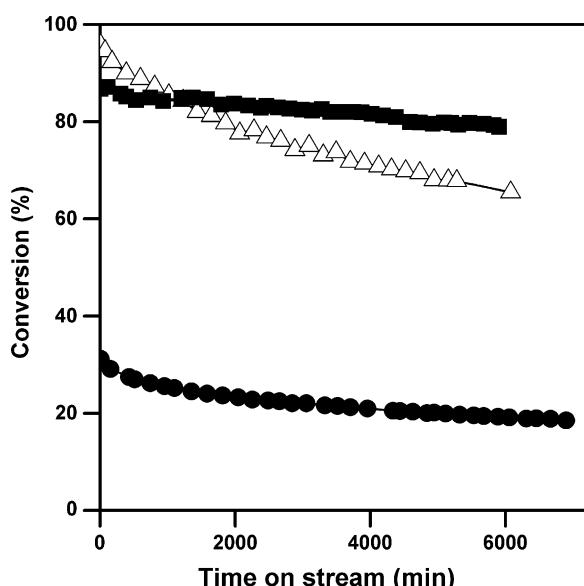


Fig. 9. Evolution of chloromethanes conversion upon time on stream with the PdCCl catalyst: (■) TCM; (△) DCM; (●) MCM.

Table 4
Evolution of selectivity upon time on stream (experiments of Fig. 9).

Starting chloromethane	Reaction product	Selectivity (%)		
		<i>t</i> _{os} = 10 h	<i>t</i> _{os} = 50 h	<i>t</i> _{os} = 90 h
TCM	CH ₄	48.3	52.6	53.8
	C ₂ H ₆	32.5	31.3	30.9
	C ₂ H ₄	0.3	0.0	0.0
	C ₃ H ₈	10.1	8.6	8.2
	CH ₃ Cl	5.7	5.0	4.8
	CH ₂ Cl ₂	3.1	2.5	2.3
DCM	CH ₄	67.8	71.8	71.7
	C ₂ H ₆	20.3	15.6	15.5
	C ₃ H ₈	1.6	1.3	1.3
	CH ₃ Cl	10.3	11.3	11.5
MCM	CH ₄	100.0	100.0	100.0

metal surface. Deposition of hydrocarbons does not appear to be the cause because in that case it should be expected a greater deactivation in the hydrodechlorination of TCM as it leads to much higher amounts of hydrocarbon products. On the other hand, the analysis of the Cl 2p XPS spectra of the catalysts (Fig. 3) showed a considerably increase of organic chloride upon use, suggesting that poisoning by chlorinated species may be occurring. This could also explain the fact that deactivation of the catalyst is more pronounced in the HDC of DCM. The intermediate reactivity of DCM can explain its higher poisoning effect. The high reactivity of TCM favours its hydrogenation and formation of condensation products thereby inhibiting the irreversible chemisorption. The lower reactivity of MCM suggests a lower degree of chemisorption. DCM must be more strongly chemisorbed than MCM, but it is not as reactive as to give rise to a wide diversity of hydrocarbon products upon reaction with other adsorbed radicals, as is the case of TCM.

Very few studies of deactivation of supported metal catalysts in the hydrodechlorination of chloromethanes can be found so far in the literature. However some studies dealing with the hydrodechlorination of other compounds have proposed that the formation of carbonaceous deposits, including chlorine in their constitution in many cases, is one of the main causes of deactivation of these catalysts [31,37,38].

Table 4 shows the evolution of the products distribution upon time on stream. As can be observed, in general, no significant variations of selectivity take place with time on stream. Methane and chloromethanes selectivities (these latter in TCM HDC) slightly increase with time on stream while those of hydrocarbons higher than C₁ slightly decrease. This is consistent with the causes of deactivation discussed before. The poisoning of electrodeficient Pd active sites where the chloromethanes are adsorbed reduces the possibility of reaction for these species.

4. Conclusions

Pd on activated carbon catalysts have been prepared showing fairly high activity in the deep gas-phase hydrodechlorination of MCM, DCM and TCM, the reactivity following the order CHCl₃ > CH₂Cl₂ > CH₃Cl. Selectivities to non-chlorinated compounds were found to be higher than 90% in most cases. Methane is the only reaction product obtained in the HDC of MCM while a wider diversity of reaction products is formed as the chlorine content of the starting chloromethane increases. The analysis of the evolution of yield and selectivities to reaction products with space-time in the HDC of TCM with the catalyst prepared from PdCl₂ suggests that all are primary products. CH₄, CH₃Cl and CH₂Cl₂ come from the hydrogenation of the corresponding adsorbed chloride radical, while hydrocarbons of more than one carbon atoms are formed by reaction and subsequent hydrodechlorination

of two radicals adsorbed in neighbouring active sites. The catalyst undergoes a significant deactivation in the HDC of MCM and DCM, especially with the latter whereas it remains more stable in the case of TCM. Deactivation may be due to a great decrease of the accessible metal surface which can be attributed to the poisoning of active centers by chlorinated hydrocarbons. The use of $\text{Pd}(\text{NO}_3)_2$ as Pd precursor leads to a decrease in the activity of the catalyst due to its lower Pd dispersion and a lower proportion of electrodeficient Pd.

Acknowledgements

The authors gratefully acknowledge financial support from the Spanish MEC through the project CTQ2005-07579. M.A. Álvarez Montero also wishes to thank the Spanish MEC for her research grant.

References

- [1] Z.M. de Pedro, L.M. Gomez-Sainero, E. Gonzalez-Serrano, J.J. Rodriguez, Ind. Eng. Chem. Res. 45 (2006) 7760–7766.
- [2] E.D. Goldberg, Sci. Total Environ. 100 (1991) 17–28.
- [3] M. Tancrede, R. Wilson, L. Zeise, E.A.C. Crouch, Atmos. Environ. 21 (1987) 2187–2205.
- [4] W.J. Hayes, E.R. Laws, *Handbook of Pesticide Toxicology*, Academic Press, San Diego, 1991.
- [5] S. Ordonez, H. Sastre, F.V. Diez, Appl. Catal. B-Environ. 25 (2000) 49–58.
- [6] M. Legawiec-Jarzyna, A. Srebowata, W. Juszczak, Z. Karpinski, React. Kinet. Catal. Lett. 87 (2006) 291–296.
- [7] H.M. Chiang, J.W. Bozzelli, Combust. Fundam. Appl. Jt. Tech. Meet., Cent. East. States Sect. Combust. Inst. (1993) 322–324.
- [8] A.H. Weiss, B.S. Gambhir, R.B. Leon, J. Catal. 22 (1971) 245.
- [9] A.H. Weiss, S. Valinski, G.V. Antoshin, J. Catal. 74 (1982) 136–143.
- [10] H.C. Choi, S.H. Choi, O.B. Yang, J.S. Lee, K.H. Lee, Y.G. Kim, J. Catal. 161 (1996) 790–797.
- [11] H.C. Choi, S.H. Choi, J.S. Lee, K.H. Lee, Y.G. Kim, J. Catal. 166 (1997) 284–293.
- [12] E.S. Lokteva, V.I. Simagina, E.V. Golubina, I.V. Stoyanova, V.V. Lunin, Kinet. Catal. 41 (2000) 776–781.
- [13] Y.C. Cao, X.Z. Jiang, J. Mol. Catal. A-Chem. 242 (2005) 119–128.
- [14] J. Góralski, B. Szczepaniak, J. Grams, W. Maniukiewicz, T. Paryjczak, Pol. J. Chem. Technol. 9 (2007) 77–80.
- [15] S.Y. Kim, H.C. Choi, O.B. Yang, K.H. Lee, J.S. Lee, Y.G. Kim, J. Chem. Soc. Chem. Commun. (1995) 2169–2170.
- [16] E. Lopez, S. Ordonez, F.V. Diez, Appl. Catal. B-Environ. 62 (2006) 57–65.
- [17] T. Mori, K. Hirose, T. Kikuchi, J. Kubo, Y. Morikawa, J. Jpn. Pet. Inst. 45 (2002) 256–259.
- [18] E. Lopez, S. Ordonez, H. Sastre, F.V. Diez, J. Hazard. Mater. 97 (2003) 281–294.
- [19] L. Prati, M. Rossi, Appl. Catal. B-Environ. 23 (1999) 135–142.
- [20] A. Malinowski, D. Lomot, Z. Karpinski, Appl. Catal. B-Environ. 19 (1998) L79–L86.
- [21] T. Mori, T. Kikuchi, J. Kubo, Y. Morikawa, Chem. Lett. (2001) 936–937.
- [22] B. Aristizabal, C.A. Gonzalez, I. Barrio, M. Montes, C.M. de Correa, J. Mol. Catal. A-Chem. 222 (2004) 189–198.
- [23] C.A. Gonzalez, M. Bartoszek, A. Martin, C. Montes de Correa, Ind. Eng. Chem. Res. 48 (2009) 2826–2835.
- [24] L.M. Gomez-Sainero, X.L. Seoane, J.L.G. Fierro, A. Arcoya, J. Catal. 209 (2002) 279–288.
- [25] C.D. Wagner, L.E. Davis, M.V. Zeller, J.A. Taylor, R.H. Raymond, L.H. Gale, Surf. Interface Anal. 3 (1981) 211–225.
- [26] S.H. Ali, J.G. Goodwin, J. Catal. 176 (1998) 3–13.
- [27] N. Mahata, V. Vishwanathan, Catal. Today 49 (1999) 65–69.
- [28] S. Sombroonthanakij, O. Mekasuwandumrong, J. Panpranot, T. Nimmanwuttipong, R. Strobel, S.E. Pratsinis, P. Praserthdam, Catal. Lett. 119 (2007) 346–352.
- [29] J.L. Gasser-Ramirez, B.C. Dunn, D.W. Ramirez, E.P. Fillerup, G.C. Turpin, Y. Shi, R.D. Ernst, R.J. Pugmire, E.M. Eyring, K.A. Pettigrew, D.R. Rolison, J.M. Harris, J. Non Cryst. Solids 354 (2008) 5509–5514.
- [30] P.A. Simonov, E.M. Moroz, A.L. Chuvalin, V.N. Kolomiichuk, A.I. Boronin, V.A. Likholobov, Preparation of Catalysts VI—Scientific Bases for the Preparation of Heterogeneous Catalysts, vol. 91, 1995, pp. 977–987.
- [31] S. Ordonez, F.V. Diez, H. Sastre, Appl. Catal. B-Environ. 31 (2001) 113–122.
- [32] L.M. Gomez-Sainero, X.L. Seoane, A. Arcoya, Appl. Catal. B-Environ. 53 (2004) 101–110.
- [33] J.M. Thomas, W.J. Thomas, *Introduction to the Principles of Heterogeneous Catalysts*, Academic Press, New York, 1969.
- [34] J.L. Seoane, P. Bouthy, R. Montarnal, J. Catal. 63 (1980) 182–190.
- [35] E.G. Derouane, *Zeolites: Science and Technology*, Martinus Nijhoff Publisher, The Hague, 1984.
- [36] G. Centi, *Elementary Reaction Steps in Heterogeneous Catalysis*, Kluwer Academic Publishers, Dordrecht, The Nederlands, 1993.
- [37] T. Mori, T. Yasuoka, Y. Morikawa, Catal. Today 88 (2004) 111–120.
- [38] N.C. Concibido, T. Okuda, W. Nishijima, M. Okada, Appl. Catal. B-Environ. 71 (2007) 64–69.